

Structural, electronic and magnetic properties of SrRuO₃ under epitaxial strain

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Using density functional theory within the local spin density approximation, structural, electronic and magnetic properties of SRO are investigated. We examine the magnitude of the orthorhombic distortion in the ground state and also the effects of applying epitaxial constraints, whereby the influence of large (in the range of $\pm 4\%$) in-plane strain resulting from coherent epitaxy, for both [001] and [110] oriented films, have been isolated and investigated. The overall pattern of the structural relaxations reveal coherent distortions of the oxygen octahedra network, which determine stability of the magnetic moment on the Ru ion. The structural and magnetic parameters exhibit substantial changes allowing us to discuss the role of symmetry and possibilities of magneto-structural tuning of SrRuO₃-based thin film structures.

I. INTRODUCTION

Epitaxial thin film technology has the potential to change the functionality of conventional crystals in a way to achieve better performance and novel properties. Grown layer by layer in thin film geometries, the crystals still retain their bulk-like properties in two in-plane lateral dimensions, while being strongly modified along the direction of growth by finite-size effects, presence of interfaces and surfaces, and the misfit strain from epitaxial lattice-matching. Additional interactions which emerge between consequent layers allow control, tuning and enhancing of their functional properties. Complex artificially-designed heterostructures with specific characteristics can be synthesized with atomic-level precision [1].

In many perovskite-oxide based heterostructures and superlattices, the metallic ferromagnetic perovskite SrRuO₃ plays a particularly key role, often serving as an electrode material that allows for better integration and facilitates electrical measurements [2, 3]. However, recent studies of epitaxial thin films [4] suggest that SrRuO₃ may have novel magnetostructural properties in ultra-thin film form. By tuning film thickness and in-plane strain (through choice of substrate) very different properties may emerge as compared with the bulk. Similar approaches have been exploited in recent experimental and theoretical investigations showing modifications of the ferroelectric epitaxial thin films with strongly enhanced performance [5–9]. However, to our knowledge, the impact of strain on ferromagnetic perovskite films has not yet been studied.

Bulk SrRuO₃ undergoes a series of phase transformations with decreasing temperature (for more details see Ref. [10, 11]). It is a metallic ferromagnet with a Curie

temperature about 160 K and a magnetic moment of 1.1 μ_B per formula unit [12]. The ideal cubic perovskite structure with cubic symmetry $Pm\bar{3}m$ is stable above 950 K. From this temperature and down to 820 K it appears in the tetragonal $I4/mcm$ structure. Below 850 K and at standard pressures, SrRuO₃ has an orthorhombically distorted perovskite structure (space group $Pbnm$ [41] with 20 atoms per cell [13]). The structure is the GdFeO₃/CaTiO₃-type, which can be understood by first doubling the 5-atom cell along [110] with both oxygen octahedra being rotated in the same way around [001] (z -axis), and then doubling this 10-atom system along [001] with two oxygen octahedra connected along the z -axis, being further tilted in opposite directions. This structure is shown in Fig 1. In the Glazer notations, the tilting of SrRuO₃ is described by $(a^-a^-c^+)$ [14, 15]. One of our main points below will be that in SrRuO₃, the rotation and tilting is accompanied by a substantial deformation of the oxygen octahedra.

Previous first-principles studies of SrRuO₃ examined the electronic and magnetic properties of the bulk low-temperature $Pbnm$ structure [16–18]. Their results largely agree with experimental observations and explain basic features of the ground state in the absence of strain. In this paper, we use first-principles calculations to isolate and investigate the effect of epitaxial strain on the structure of SrRuO₃. We explore SrRuO₃ with this constraint through examination of the orthorhombic distortion, magnetic and electronic properties of the $Pbnm$ structure, elucidating the differences between bulk and epitaxially strained thin films in the [001] and [110] orientations.

In section II we give a short description of our methods used in this work. Section III presents our most important results, which we split into two parts. In part (A) we concentrate on the structural parameters of a strain-free structure and highlight a confusion in the literature about the lattice parameters of SrRuO₃. Part (B) deals with [001] and [110] oriented structures of SrRuO₃ grown

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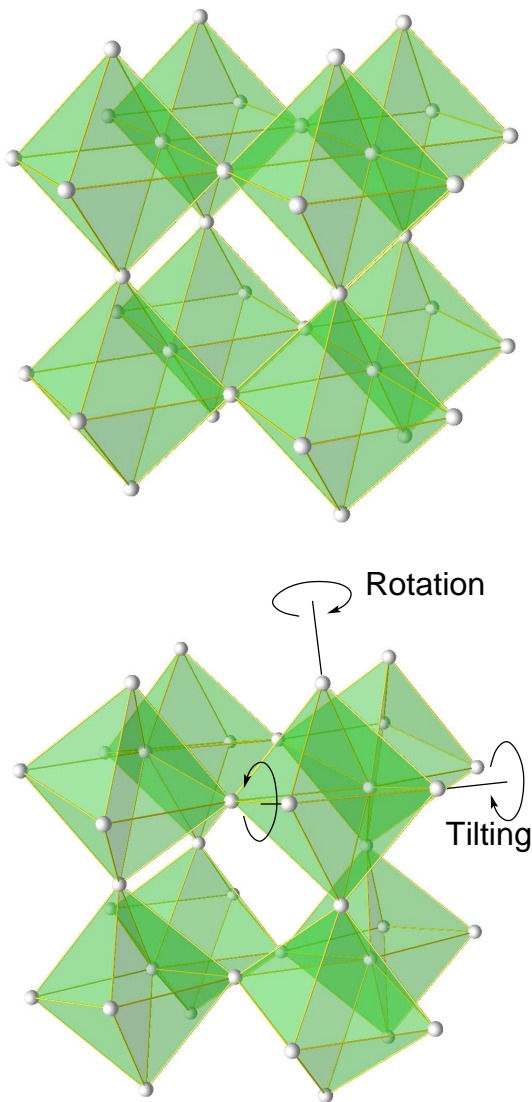


FIG. 1: (Top picture) The structure of the oxygen network in a $Pm\bar{3}m$ perovskite structure. The oxygen octahedra are perfectly regular. (Bottom picture) The structure of orthorhombic $Pbnm$ perovskite structure with tilting (rotation of the octahedral cages). The oxygen octahedra in this case are not necessary regular. We consider this aspect in section III of this paper.

with tensile and compressive misfit strain. Section IV presents discussions of three selected topics which follow from our results and deserve more attention. Conclusions are given in Section V.

II. METHODS

All calculations are performed with the Vienna *ab-initio* Simulations Package (VASP) [19, 20], with the Ceperley-Alder parametrization of the local spin-density approximation (LSDA) and projector-augmented wave

potentials [21, 22]. The calculations are performed using a plane-wave energy cutoff of 500 eV and the convergence was checked with a cutoff of 600 eV. For calculations with the $Pbnm$ unit cell of SrRuO_3 , which contains 4 formula units (f.u.) or 20 atoms per cell, a $12 \times 12 \times 10$ Monkhorst-Pack k -point mesh is found to yield convergence of all properties computed here and is used in all self-consistent calculations. For a simple cubic perovskite cell with 5 atoms we used a $12 \times 12 \times 12$ k -point sampling.

In order to isolate the effects of epitaxial strain, we perform bulk calculations of the $Pbnm$ ground-state structure with lattice vectors constrained to match a hypothetical substrate. Specifically, for a series of values of misfit strain, we fix the in-plane (xy plane) lattice vectors, allowing the c lattice parameter (perpendicular to the substrate) and the internal ionic coordinates to fully relax within the symmetry of the $Pbnm$ space group. The ions were free to move until the Hellmann-Feynman forces were less than 4 meV/Å.

Two different angles characterize the degree of rotation and tilting of the oxygen octahedra in SrRuO_3 . The rotation and tilting represent basically the same type of distortion, but with respect to different directions. It is conventional to define the rotation along the z axis separately from those along the x and y axes, referred to as tiltings. For what follows, we define the dihedral angle Θ to be along the $\text{Ru}_1\text{-O}_2\text{-Ru}_3$ bond shown in Fig. 2, and the tilting angle is given by $(180-\Theta)/2$. Similarly, the

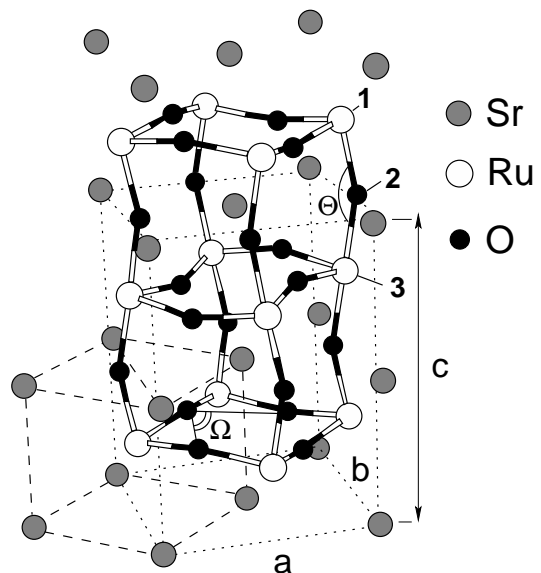


FIG. 2: The $Pbnm$ crystal structure of SrRuO_3 ($\text{GdFeO}_3/\text{CaTiO}_3$ -type). The unit cell consists of four formula units of the ideal cubic perovskite structure. The Ru atoms possess relatively large magnetic moments and occupy high-symmetry positions in the orthorhombic unit cell. The atoms of oxygen and Sr are displaced from their high-symmetry positions due to the tilting. The numbers attached to certain atoms help us to define the angle of tilting as discussed in the section “Methods”.

III. RESULTS

A. Strain-free structure of SrRuO₃

Starting from the experimental space group $Pbnm$, we first obtain the ground state structure of SrRuO₃ by relaxing all seven free internal structural parameters (internal atomic coordinates) and three lattice parameters. Our results, along with a comparison with the experimental values for different perovskite systems, are shown in Tables I and II. The calculated parameters are in good agreement with experiment. The slight underestimate of the lattice constant is typical for LSDA. We calculate the FM state in $Pbnm$ structure to have an energy 186 meV/f.u. lower than that of the cubic perovskite FM system, which was optimized within the $Pm\bar{3}m$ symmetry (see Table III). A previous first-principles study (Ref. 16) computed a comparable energy difference, 140 meV/f.u., using structures with experimental lattice parameters.

Experimental values of the magnetic moment in SrRuO₃ range between 1.1 and 1.6 μ_B /f.u.; the spread in values is expected given the difficulty of making single-domain samples and their large magnetocrystalline anisotropy [12, 23]. According to Ref. 18, only approximately 60% of the total magnetic moment is Ru derived, while the remaining 40% is distributed among oxygen sublattice sites. A similar spread of the values of the magnetic moment in SrRuO₃ has been reported from theoretical investigations. Usually they are obtained using the LSDA and experimental lattice parameters for the orthorhombic $Pbnm$ structure. Such calculations reported magnetic moments ranging between 0.97 and 1.96 μ_B /f.u. [16, 17, 24, 25]

With an intermediate degree of relaxation, keeping the experimental lattice parameters fixed, but allowing the Wyckoff positions to change, we obtain 1.2 μ_B /f.u. After a complete relaxation of the structure, our magnetic moment calculated with LSDA is 0.98 μ_B /f.u., smaller than that obtained with experimental lattice parameters, as would be expected with the smaller LSDA lattice parameters. A summary of all calculated lattice parameters appears in Table II. The LSDA slightly overestimates bond strength and therefore favors stronger hybridization of the Ru- d and O- p states, giving smaller lattice parameters and consequently smaller magnetic moments.

In addition to the ferromagnetic (FM) configuration, we optimize the bulk structural parameters of SRO with different initial magnetic orderings, including the non-magnetic (NM) phase and three different antiferromagnetic (AFM) spin arrangements. Several local minima in the total energy are found. Among these minima, the FM configuration is computed to be the most stable state, in agreement with experiment. The A-type AFM and C-type AFM, and NM configurations are found to be 6.77 meV/f.u., 6.44 meV/f.u., and 8.15 meV/f.u. higher in energy than the FM ground state, respectively. The G-type AFM configuration is found to be unstable: when relaxed, it reverts to the NM minimum. In the remaining

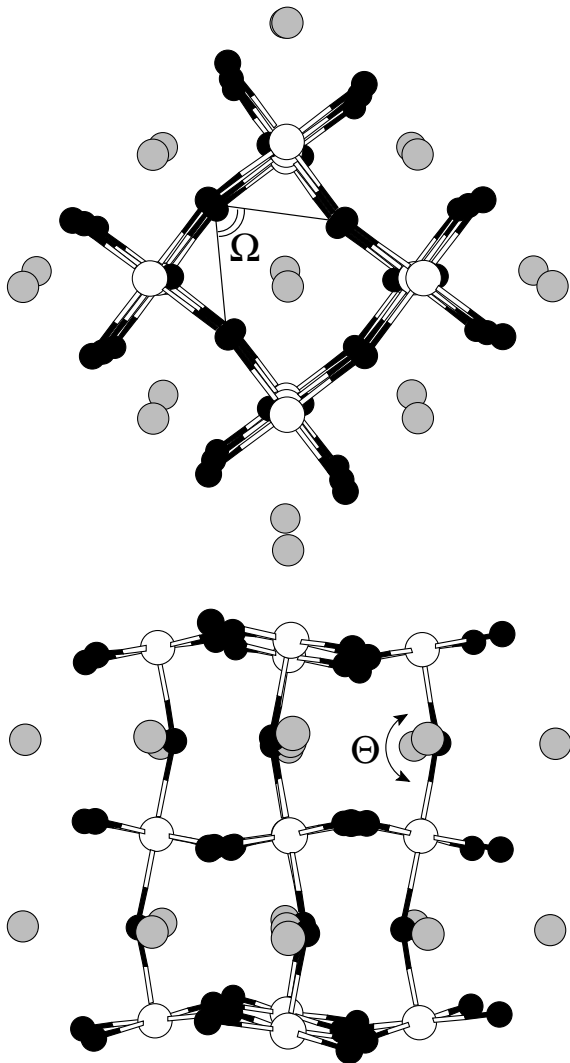


FIG. 3: (Top picture) The top view of the structure of SrRuO₃ showing the distortion which we refer to as a rotation. The corner-connected oxygen octahedra rotate in opposite directions around the [001] direction. This distortion changes the a and b parameters of the structure equally. (Bottom picture) The tilting of the SrRuO₃ structure shown projected along the [110] direction (or b axis of the $Pbnm$ structure). In this view one can see the folding of the [001] plane that is responsible for the shrinking of the $Pbnm$ structure along the a axis.

rotation angle is defined through the relation $(90-\Omega)/2$, where Ω is an angle shown in Figures 2 and 3. The rotation and tilting commute with each other and uniquely describe the network of oxygen octahedra, assuming the octahedrons are regular. We will return to the validity of this assumption later in section III [42].

TABLE I: Experimental structural parameters for several perovskite systems with $Pbnm$ symmetry taken from Ref. 13, 26–30. We focus in this list on the relations of the a , b and c lattice parameters. In most of the systems $a < b$ is satisfied due to the tilting of the oxygen octahedra, whereby only the a vector shrinks, while the b vector remains unchanged. From this table, one can see that for SrRuO_3 the ratio $a < b$ is not satisfied.

| | $a(\text{\AA})$ | $b(\text{\AA})$ | $c(\text{\AA})$ | Wyckoff position | x | y | z |
|------------------|-----------------|-----------------|-----------------|------------------|---------|--------|--------|
| SrRuO_3 | 5.5670 | 5.5304 | 7.8446 | Sr (4c) | -0.0027 | 0.0157 | 0.25 |
| | | | | Ru (4b) | 0.5 | 0.0 | 0.0 |
| | | | | O (8d) | 0.7248 | 0.2764 | 0.0278 |
| | | | | O (4c) | 0.0532 | 0.4966 | 0.25 |
| GdFeO_3 | 5.3510 | 5.6125 | 7.6711 | Gd (4c) | -0.0015 | 0.0626 | 0.25 |
| | | | | Fe (4b) | 0.5 | 0.0 | 0.0 |
| | | | | O (8d) | 0.6966 | 0.3011 | 0.0518 |
| | | | | O (4c) | 0.1009 | 0.4669 | 0.25 |
| GdAlO_3 | 5.2537 | 5.3030 | 7.4434 | Gd (4c) | -0.0079 | 0.0376 | 0.25 |
| | | | | Al (4b) | 0.5 | 0.0 | 0.0 |
| | | | | O (8d) | 0.7147 | 0.2855 | 0.0387 |
| | | | | O (4c) | 0.0724 | 0.4863 | 0.25 |
| CaTiO_3 | 5.3804 | 5.4422 | 7.6417 | Ca (4c) | -0.0065 | 0.0349 | 0.25 |
| | | | | Ti (4b) | 0.5 | 0.0 | 0.0 |
| | | | | O (8d) | 0.7111 | 0.2884 | 0.0372 |
| | | | | O (4c) | 0.0707 | 0.4842 | 0.25 |
| CaRuO_3 | 5.3408 | 5.5311 | 7.6460 | Ca (4c) | -0.0150 | 0.0560 | 0.25 |
| | | | | Ru (4b) | 0.5 | 0.0 | 0.0 |
| | | | | O (8d) | 0.6930 | 0.2970 | 0.0530 |
| | | | | O (4c) | 0.0910 | 0.4670 | 0.25 |
| GdScO_3 | 5.4862 | 5.7499 | 7.9345 | Gd (4c) | -0.0163 | 0.0594 | 0.25 |
| | | | | Sc (4b) | 0.5 | 0.0 | 0.0 |
| | | | | O (8d) | 0.6931 | 0.3007 | 0.0556 |
| | | | | O (4c) | 0.1183 | 0.4465 | 0.25 |
| DyScO_3 | 5.4400 | 5.7130 | 7.887 | Dy (4c) | -0.0172 | 0.0607 | 0.25 |
| | | | | Sc (4b) | 0.5 | 0.0 | 0.0 |
| | | | | O (8d) | 0.6926 | 0.3040 | 0.0608 |
| | | | | O (4c) | 0.1196 | 0.445 | 0.25 |

TABLE II: Calculated structural parameters for several perovskite systems with $Pbnm$ symmetry. Theoretical results also show the distortion of SrRuO_3 for which the orthorhombic distortion is opposite to other perovskites. We introduce parameters, Δa and Δb , which characterize shrinking of the a and b lattice parameters, respectively. The parameter a shrinks due to the tilting, while b shrinks due to the rectangular distortion of the horizontal middle plane of the oxygen octahedra.

| | $a(\text{\AA})$ | $b(\text{\AA})$ | $c(\text{\AA})$ | Wyckoff pos. | x | y | z | Tilting | Δa | Δb |
|------------------|-----------------|-----------------|-----------------|--------------|---------|--------|--------|---------------|------------|------------|
| SrRuO_3 | 5.5031 | 5.4828 | 7.7546 | Sr (4c) | -0.0050 | 0.0296 | 0.25 | 10.21° | 1.58 | 1.75 |
| | | | | Ru (4b) | 0.5 | 0.0 | 0.0 | | | |
| | | | | O (8d) | 0.7165 | 0.2834 | 0.0336 | | | |
| | | | | O (4c) | 0.0647 | 0.4941 | 0.25 | | | |
| CaRuO_3 | 5.2090 | 5.5297 | 7.5512 | Ca (4c) | -0.0211 | 0.0645 | 0.25 | 16.79° | 4.26 | 2.15 |
| | | | | Ru (4b) | 0.5 | 0.0 | 0.0 | | | |
| | | | | O (8d) | 0.6929 | 0.2996 | 0.0519 | | | |
| | | | | O (4c) | 0.1034 | 0.4665 | 0.25 | | | |
| CaTiO_3 | 5.2900 | 5.4007 | 7.5334 | Ca (4c) | -0.0099 | 0.0468 | 0.25 | 13.26° | 2.67 | 0.75 |
| | | | | Ti (4b) | 0.5 | 0.0 | 0.0 | | | |
| | | | | O (8d) | 0.7065 | 0.2926 | 0.0425 | | | |
| | | | | O (4c) | 0.0811 | 0.4790 | 0.25 | | | |

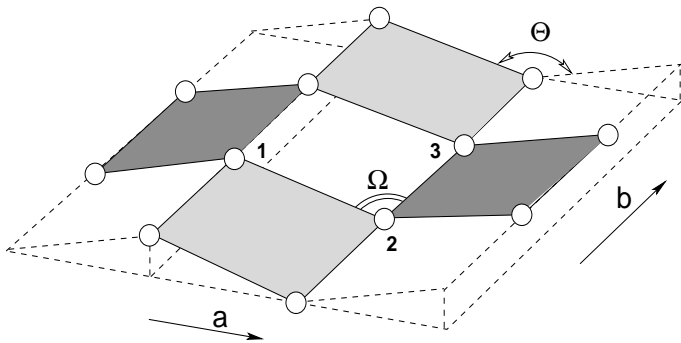


FIG. 4: This picture illustrates schematically the fact that as a result of tilting the $Pbnm$ structure is necessarily orthorhombic. This appears from simple geometrical considerations when tiltings a^-a^- have the effect of folding of the Ru-O (001) atomic planes. If the folding develops along the a axis, while another lattice vector b remains unchanged, we have $a < b$. The importance of this point can be seen when the $Pbnm$ structure is subject to the epitaxial constraints enforcing $a = b$. The rotation around the z axis is different because it changes the a and b parameters of the $Pbnm$ structure in equal proportions. So, the $a = b$ constraint requires the middle plane of the oxygen octahedra to shrink along the b axis. In order to characterize this epitaxially constrained structure we introduce the notation $e\text{-}Pbnm$. The angles shown define degrees of tilting and rotation as discussed in the section “Methods”.

of this paper, we focus on the FM state and its comparison with the NM state.

At this point, we turn to a discussion of the lattice parameters of the $Pbnm$ structure. From Tables I and II, we can see that most of the $Pbnm$ GdFeO_3 -type structures have $a < b < c$. Interestingly, however, in the case of SrRuO_3 this relation is not satisfied. SrRuO_3 is the only compound we know of for which this is the case. This has led to a confusion in the literature where one can find reports both of $a > b$ (see Refs.11, 13, 31–33) and $a < b$ (see Refs.23, 24, 34, 35); in the latter case parameters are apparently switched to be consistent with overall trend in the GdFeO_3 -type structures. To clarify the unique situation in SrRuO_3 other geometrical factors making up the orthorhombic distortions of the $Pbnm$ structure need to be considered, as we now explain.

Figure 3, together with a sketch in Fig.4, illustrates the relationship between octahedral tilting and rotation and the orientations of the interatomic bonds. The in-plane lattice parameters of the $Pbnm$ structure are not equal, that is $a \neq b$, as a consequence of the tilting; the rotation on the other hand does not change the ratio of a to b . For arrangements with $Pbnm$ symmetry, if the octahedra were regular, tilting would require $a < b$, and not the other way around. This simple geometrical picture explains the orthorhombic shape of most of the known perovskite systems listed in Table I, with the notable exception of SrRuO_3 .

Our theoretical calculations confirm that for SrRuO_3 , $a > b$ (see Tab. II), while for the systems like CaRuO_3

and CaTiO_3 , $a < b$. An analysis of the results of our calculations shows that the reason for the apparent anomaly in SrRuO_3 is that the oxygen octahedra are not regular: the “horizontal” middle plane is not square, but rather is rectangular. The rectangular distortion occurs along the b axis partially compensating the orthorhombic distortion originating with the tilting. Thus, two different contributions determine the orthorhombic distortion (the a/b ratio) in the $Pbnm$ structure.

In Table II we summarize the impact of distortions coming from each contribution. The anomalous orthorhombic distortion in SrRuO_3 is derived from geometrical considerations and those parameters which we already have: a , b , c , tilting and rotation angles. If a^{oct} and b^{oct} describe the equatorial plane of the octahedra, then the lattice parameters of $Pbnm$ can be expressed as follows:

$$\begin{cases} a = 2a^{\text{oct}} \cos(\text{rotation}) \cos(\text{tilting}); \\ b = 2b^{\text{oct}} \cos(\text{rotation}). \end{cases} \quad (1)$$

Consequently, the orthorhombic distortion can be expressed as:

$$\frac{a}{b} = \left[\frac{a^{\text{oct}}}{b^{\text{oct}}} \right] \cos(\text{tilting}). \quad (2)$$

These simple relations show that the internal distortions can be readily determined from fundamental parameters of the $Pbnm$ structure. However, it is important to note that the oxygen octahedra are not necessarily regular, i.e. a^{oct} and b^{oct} are free parameters unique for each material.

B. Epitaxially constrained structure: $e\text{-}Pbnm$

We now consider the structure and properties of epitaxially strained $Pbnm$ SrRuO_3 . Experimentally, SrRuO_3 films can grow with either [001] or [110] orientations on various substrates like LaAlO_3 , SrTiO_3 , DyScO_3 or GdScO_3 [33, 34] (see Ref. 35 for good illustrations of the two geometries). The [001] case is a relatively straightforward extension of previously studied perovskite multi-layers [36, 37], except that additional degrees of freedom must be considered to account for the tilting and rotation. In the [110] orientation, the situation is quite different, as we discuss in detail below.

1. Geometries of the [001] and [110] oriented films

For the [001] oriented films, the a and b parameters of the orthorhombic $Pbnm$ lattice are constrained to be equal (in order to match the square lattice of the substrate). We refer to these constrained structures, with all other structural parameters relaxed, as $e\text{-}Pbnm[001]$,

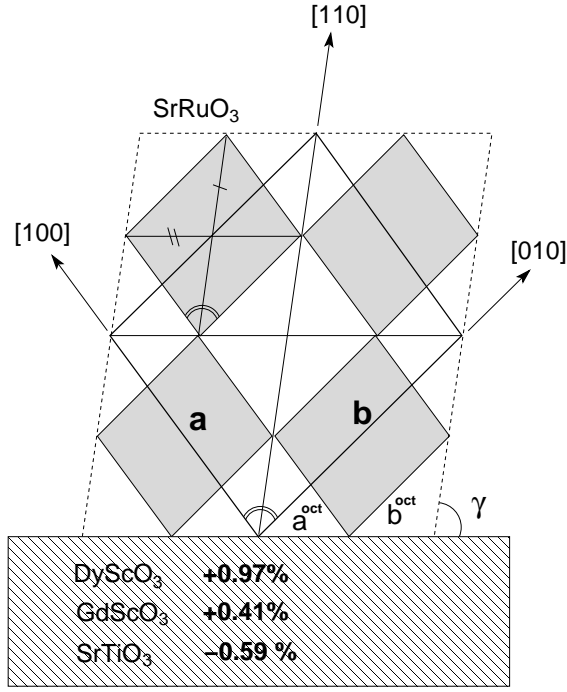


FIG. 5: Schematic presentation of the epitaxial structure of SrRuO₃ grown in the [110] orientation. The grey parallelograms represent the equatorial planes of the oxygen octahedra in the (001) plane. This geometry implies that at zero in-plane strain the structure still have the orthorhombic symmetry, but its [110] direction is not normal to the substrate. Due to the orthorhombic symmetry, there is an angle γ defined by eq.(3). Applying in-plane strain changes this angle, but at the same time the orthorhombic symmetry is broken. SrRuO₃ grown with the [110] orientation under strain is monoclinic.

where “e” indicates “epitaxial”. Misfit strain is measured relative to the lowest energy *e-Pbnm*[001] structure, the computed parameters being given in Table III. Note that the zero misfit strain structure is not the same as the strain-free structure discussed in the previous subsection, as the latter is not compatible with the epitaxial constraints. For the *e-Pbnm* structure we have $\Delta a = \Delta b$ (from Table II), i.e. two kinds of distortions compensate each other, as they are forced to by the imposed conditions.

In the [110] orientation, we consider a general case when the SrRuO₃ film is grown on an orthorhombic substrate. We assume that our substrate has in-plane non-equal lattice parameters, but they are kept orthogonal. If we made the in-plane parameters equal, this would correspond, for example, to a cubic lattice of SrTiO₃ with a compressive lattice mismatch of about 0.59%. But making the in-plane lattice rectangular brings us close to the situation with GdScO₃ or DyScO₃ substrates, whose structures match nicely with [110] oriented structure of SrRuO₃ (we refer to it as *e-Pbnm*[110], although we show that it may have lower symmetry). In this case SrRuO₃ is subject to substantially different constraints compared

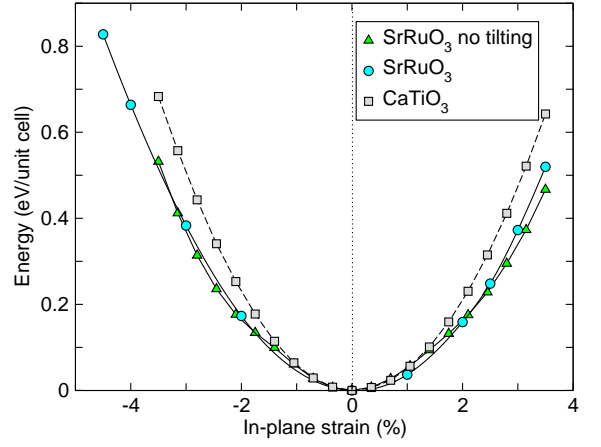


FIG. 6: The comparison of the elastic energies of FM *e-Pbnm*[001] SrRuO₃ and NM *e-Pbnm*[001] CaTiO₃ as a function of the applied misfit strain. The in-plane lattice parameters were fixed by the value of the misfit strain, while all other parameters of the structures were relaxed to the zero-force states. In addition we show here the total energy of the simple *P4/mmm* perovskite SrRuO₃ when rotation and tilting are not allowed. This allows us to conclude that the tilting does not change the elasticity of the structure with respect to the misfit strain.

with the [001] orientation. The diagonal $\sqrt{a^2 + b^2}$ is fixed and the lattice parameter c is the in-plane parameter. The out-of-plane lattice vector is not perpendicular to the surface (see Figure 5), because its angle with the normal to the surface is given by the difference between parameters of *Pbnm*, a and b :

$$\gamma = 2 \arctan \left(\frac{b}{a} \right) = 2 \arctan \left(\frac{b^{\text{oct}}}{a^{\text{oct}}} \cos(\text{tilting}) \right) \quad (3)$$

Although the diagonal $\sqrt{a^2 + b^2}$ is fixed on the substrate, the ratio a/b is free to change. From eq.1 we see that $b/a = (b^{\text{oct}}/a^{\text{oct}}) \cos(\text{tilting})$. At zero in-plane strain the [110]-oriented SrRuO₃ retains the bulk structure if it is grown on SrTiO₃, but not in the case of [001] oriented GdScO₃ or DyScO₃ substrates.

2. Structural changes as a function of strain

As the epitaxial constraint is varied, the shape of the cell is changed, which increases its internal energy. In Fig. 6, we plot the elastic energy of ferromagnetic SrRuO₃ for misfit strains ranging from -4.5% to +3.5%. Surprisingly, the energetic penalties for the in-plane distortion are nearly the same for both *e-Pbnm* and *P4/mmm* structures, though the latter has no internal degrees of freedom to relax and reduce the energy. Moreover, comparing these curves with another perovskite, CaTiO₃, we see that their behavior is strikingly similar. Changes of the volume are shown in Fig. 7.

TABLE III: Computed structural parameters of SrRuO_3 in the cubic perovskite (space group $Pm\bar{3}m$) and the epitaxially constrained structure $e\text{-}Pbnm[001]$ in the zero strain state. Results for both FM and NM configurations are listed in order to show that they do not have significant differences (later on, it will be shown that applying epitaxial strain yields important differences between the FM and NM cases). The Wyckoff positions for all structures refer to space group $Pbnm$.

| | $a(\text{\AA})$ | $b(\text{\AA})$ | $c(\text{\AA})$ | Wyckoff pos. | x | y | z | Tilting | Δa | Δb |
|----------------------------|-----------------|-----------------|-----------------|--------------|---------|--------|--------|---------------|------------|------------|
| $e\text{-}Pbnm(\text{FM})$ | 5.4929 | 5.4929 | 7.7514 | Sr (4c) | -0.0055 | 0.0303 | 0.25 | 10.48° | 1.67% | 1.67% |
| | | | | Ru (4b) | 0.5 | 0.0 | 0.0 | | | |
| | | | | O (8d) | 0.7160 | 0.2837 | 0.0336 | | | |
| | | | | O (4c) | 0.0650 | 0.4937 | 0.25 | | | |
| $e\text{-}Pbnm(\text{NM})$ | 5.4929 | 5.4929 | 7.7440 | Sr (4c) | -0.0051 | 0.0304 | 0.25 | 10.48° | 1.67% | 1.69% |
| | | | | Ru (4b) | 0.5 | 0.0 | 0.0 | | | |
| | | | | O (8d) | 0.7155 | 0.2842 | 0.0345 | | | |
| | | | | O (4c) | 0.0650 | 0.4945 | 0.25 | | | |
| Cubic(FM) | 5.5070 | 5.5070 | 7.7880 | Sr (4c) | 0.0 | 0.0 | 0.25 | 0.0 | 0.0 | 0.0 |
| | | | | Ru (4b) | 0.5 | 0.0 | 0.0 | | | |
| | | | | O (8d) | 0.75 | 0.25 | 0.0 | | | |
| | | | | O (4c) | 0.0 | 0.5 | 0.25 | | | |

The degree of tilting and rotation of the oxygen octahedra reflects the impact of epitaxial strain. Figure 9 shows the evolution of these angles for both $[001]$ and $[110]$ orientations. For $[110]$ the two angles decrease together. On the other hand, for the $[001]$ orientation, the angles behave oppositely: for increasing compressive or tensile strain, the rotation or tilting become more pronounced, respectively. However, we find that the angles exhibit surprising behavior under tensile strain in the NM state (discussed further below).

In addition to the orientation of the oxygen octahedra, we observe their shape is also changing. This is especially important because we have to understand the behavior of the angles in the NM case shown in Figure 9. The splitting of two Ru-Oz curves in Figure 10 can be explained by the fact that the NM configuration allows for additional tetragonal contraction of the oxygen octahedra along the z axis. This contraction manifests itself in the trend in angles shown in Fig.9. Connection of this effect with the magnetic properties of SrRuO_3 will be discussed later in Section IV.

Applying strain induces a change in volume. In the $[110]$ orientation, the volume can be modified by rotating the angle γ or by expanding (or contracting) the out-of-plane lattice parameter. The latter can be achieved only if the symmetry of the oxygen octahedra is broken. Namely, the middle plane Ru-O bonds would be required to have different length; in the case of $[001]$ oriented films they are the same (see Fig. 10). This additional lowering of the symmetry alters the electronic environment of the Ru ion leading to a drop of its magnetic moment, as shown in Fig.8. The $[110]$ oriented structure of SrRuO_3 becomes monoclinic [43] (see Fig. 5).

IV. DISCUSSIONS

From the results reported above, we selected three particular points for further discussion. Our focus here is on the magnetostructural coupling in SrRuO_3 and its dependence on the film orientation.

A. Magnetoelastic coupling

Fig. 7 exhibits some nonlinearity in the volume of the $P4/mmm$ with misfit strain, in contrast with the $e\text{-}Pbnm[001]$ structure. To understand the behavior of $P4/mmm$ it is useful to compare Figures 7 and 8. Both curves show inflection points that in Fig.7 coincide with abrupt drops in magnetic moment. Evidently, the magnetic moment, via the spin configuration of the Ru ion, stabilizes a symmetrical non-deformed shape of the oxygen octahedra. Concurrently, the in-plane strain leads to the out-of-plane lattice expansion (contraction) under the compressive (tensile) strain. At some critical strain the contraction becomes more favorable than the magnetic orbital ordering and the lattice distorts. On the other hand, in the $e\text{-}Pbnm$ structure, the tilting and rotation preserve the shape of octahedra and the magnetic orbital ordering survives.

The behavior described here suggests a strong magnetostructural interaction, which may potentially explain past experiments showing the anomalous thermal expansion of SrRuO_3 [28]. We reserve a more complete investigation for future work.

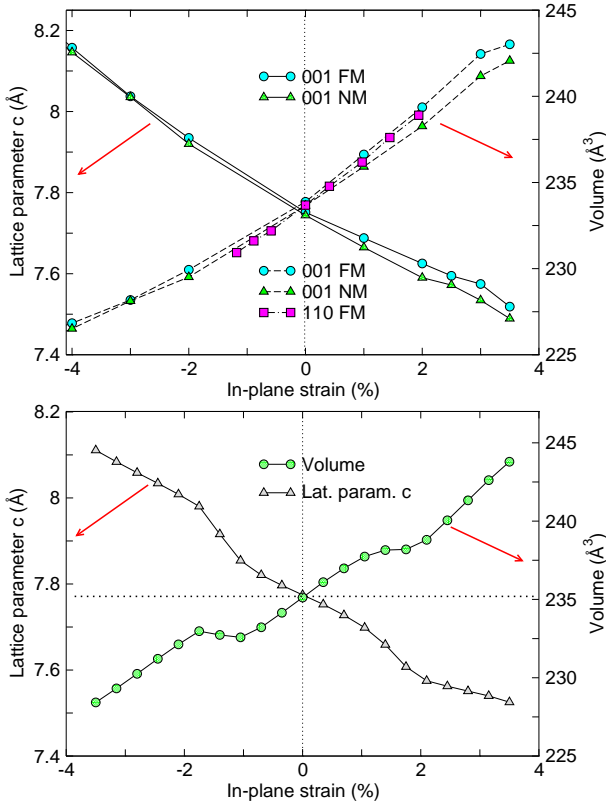


FIG. 7: Lattice parameter c and the volume of the [001] and [110] oriented perovskite structures of SrRuO_3 under epitaxial strain. (Top) The epitaxially constrained *e-Pbnm* structure. Both volume change and tetragonal distortion cost energy, whereby the structure changes these degrees of freedom simultaneously. Both [001] and [110] oriented films show similar changes in the volume as a function of the strain. (Bottom) Non-tilted [001] oriented simple perovskite *P4/mmm*. Both curves show remarkable difference of their behavior as compared to the *e-Pbnm* structure. A comparison to the Fig. 8 shows that the distortions of the *P4/mmm* are strongly influenced by the magnetoelastic coupling.

B. Anomaly of tilting and FM-NM transition

In the previous section we saw the effect of coupling between the distortions of the oxygen octahedra and the stability of the magnetic moment on Ru in the *P4/mmm* symmetry. This allows us to understand what we see in the case of *e-Pbnm*[001] structure. In Figure 10, we see an extra contraction of the Ru-O_z bond, which occurs in the NM phase under tensile strain. In contrast, in the FM phase the oxygen octahedra keep their shape by monotonically increasing the tilting angle.

This difference in the behavior of the magnetic and non-magnetic phases can be explained from a simple spin configuration argument known for SrRuO_3 [38]. If the structure is not distorted, four $4d$ electrons of Ru^{4+} occupy 3-fold degenerate t_{2g} orbitals leading to $(\uparrow t_{2g}^3, \downarrow t_{2g}^1)$, whereby two spins are not compensated and the Ru ion has a large magnetic moment. If the oxygen octahedra

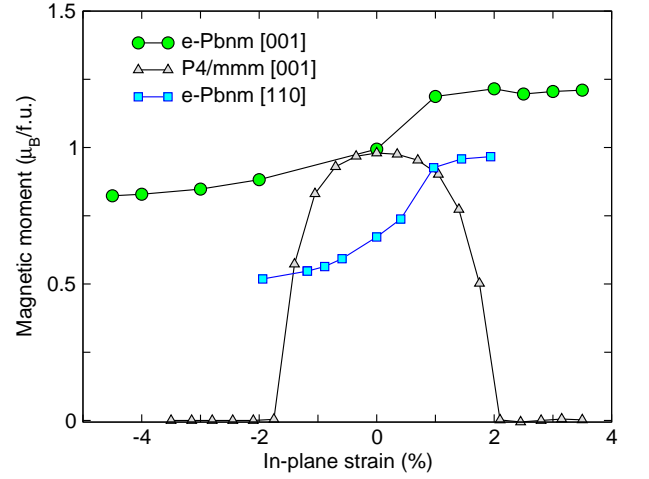


FIG. 8: The total magnetic moment of SrRuO_3 as a function of strain. In the case when tilting is not allowed (*P4/mmm*), the deformation of the Ru-O octahedra, occurring due to the strain, becomes so strong that the total magnetic moment drops down to zero. Redistribution of the electron orbitals changes the magnetic interactions. Beyond critical values of the strain, SrRuO_3 becomes non-magnetic. When the tilting is present (*Pbnm* structure) the magnetic moment is retained even at large in-plane strain. In the [110] oriented film the magnetic moment is significantly smaller, which we attribute to the geometry of the oxygen cages and the corresponding changes in the electronic structure (see DOS in Fig. 12).

are contracted along some of the Ru-O bonds, the t_{2g} orbitals split producing a non-magnetic spin configuration for Ru, $(\uparrow t_{2g}^2, \downarrow t_{2g}^2)$.

Such a transition is possible and can have significant implications for the magnetostructural tuning of the SrRuO_3 based heterostructures. One could change the magnetic ground state of SrRuO_3 by using uniaxial compression. Starting from the FM state, one can apply a uniaxial stress along the c axis. The NM state which has a shorter lattice parameter c can become the ground state. Some doping of the SrRuO_3 structure with larger atoms, like Ba, should make tilting weaker and therefore favor the NM state, i.e. reduce the amount of pressure required to transform the structure. We will discuss this issue in more detail with possible applications in our next paper.

C. Orientation dependence

We now comment on the differences between [001]- and [110]-oriented films. For the [001]-oriented films, the oxygen octahedra are free to rotate and tilt adopting to the changing lattice parameters. In contrast, in the [110] orientation both angles are fixed to the parameters of substrate. Moreover, we stressed above that the [110] oriented SrRuO_3 becomes monoclinic. This difference has consequences for the calculated electronic structure. We show the electronic DOS projected on the Ru sites

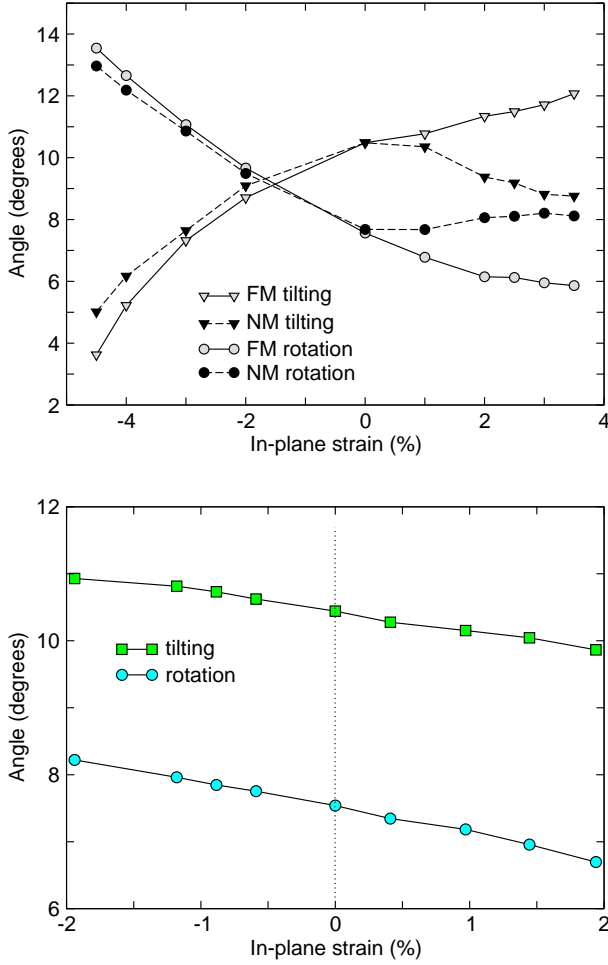


FIG. 9: Tilting and rotation angles of the oxygen octahedra as a function of strain. (Top) The $e\text{-Pbnm}[001]$ structure shows a sudden change in the behavior of the tilting and rotation angles in the NM system, which turns out to be due to the additional contraction of the oxygen octahedra along the z axis (see Fig.10). Both in the FM and NM cases under tensile strain the rotation angles stay close to a value of 10 degrees. (Bottom) In the $e\text{-Pbnm}[110]$ orientation, both angles are fixed by the substrate constraint.

for four different cases. These four plots are intended to illustrate how the electronic environment of Ru changes when distortions of the oxygen cage network occur.

The additional lowering of the symmetry in the $[110]$ orientation leads to a splitting of the t_{2g} bands associated with Ru d level, and a smaller magnetic moment (Fig.8). The gap opens at about 0.8 eV below E_F for the spin-up states, and 0.4 eV below E_F for the spin-down component (Fig. 12(Bottom)).

From examination of the electronic structure in Fig. 11 and 12 four additional features emerge. We summarize them as follows: First, for $Pm\bar{3}m$, there are no distortions of the oxygen octahedra, and thus there is no gap in DOS (see Fig. 11(Top)); second, for $Pbnm$ the octahedra are rotated, thus the t_{2g} and e_g bands start

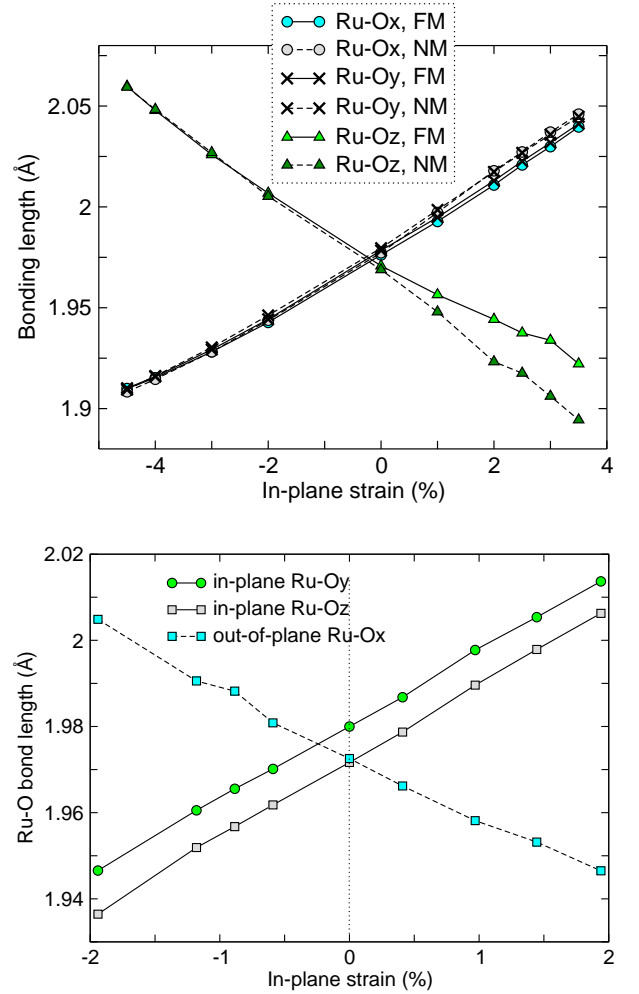


FIG. 10: Bond lengths of Ru-O inside the oxygen octahedral cages as functions of in-plane strain. (Top) The $[001]$ oriented film with FM and NM configurations. Under the tensile strain the NM and FM curves split, which is due to the additional contraction of the oxygen octahedra along the z axis in the NM case, which is reflected in smaller tilting angles shown in Fig.9. (Bottom) In the $[110]$ orientation, the substrate has an orthorhombic shape, therefore the in-plane parameters of the SrRuO_3 film are distorted. In order to be consistent we use the notations of the $[001]$ orientation. Therefore, the x axis in this case is out of plane.

to “feel” each other and repel, and as a consequence, there is a gap just above E_F in the DOS (see Figure 11(Bottom)); for $e\text{-Pbnm}[001]$ under tensile strain, the rotation is reduced and the $t_{2g}(xy)$ and $e_g(x^2 - y^2)$ recover their symmetry, whereby their repulsion becomes weaker, reducing the gap above E_F (see Fig. 12(Top)). Finally, for $e\text{-Pbnm}[110]$, this orientation requires further lowering of the symmetry. The crystal field splits the t_{2g} bands and opens an additional gap 0.8 eV (0.4 eV for spin-down) below the E_F .

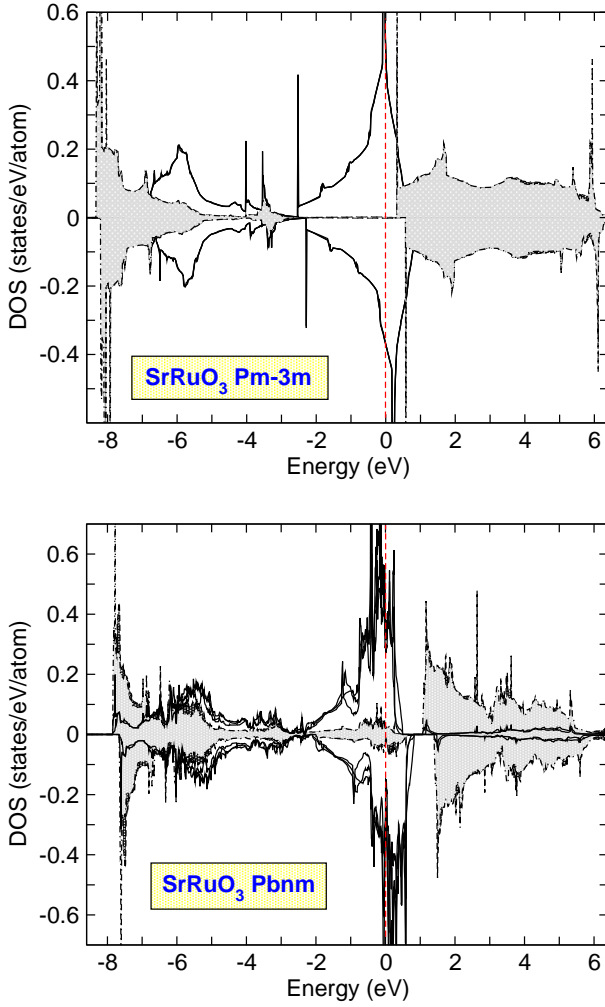


FIG. 11: Ru site projected partial DOS of SrRuO_3 . The electronic states with e_g symmetry are filled with gray color. Different orientations of the t_{2g} and e_g orbitals are plotted together without distinction in order to focus on the gaps which open when distortions are applied to the structure. (Top) DOS of the simple perovskite structure with $Pm\bar{3}m$ symmetry. There is no gap above the Fermi level. (Bottom) DOS of the strain free bulk $Pbnm$ structure. There is a gap above the Fermi level, which opens, as we discuss in the text, due to the rotations of the oxygen octahedra. In Fig. 12 it will be shown that in the $[110]$ oriented structure, one more gap opens.

V. CONCLUSIONS

In this paper, we studied properties of SrRuO_3 under conditions of epitaxial strain and different thin film orientations and considered how the changes that take place in SrRuO_3 may be used to tune properties of SrRuO_3 and SrRuO_3 based heterostructures. The results can be summarized as follows:

We explained the mechanism leading to the orthorhombic distortion of $Pbnm$, namely, the tilting and the contraction of the oxygen octahedra. The “anoma-

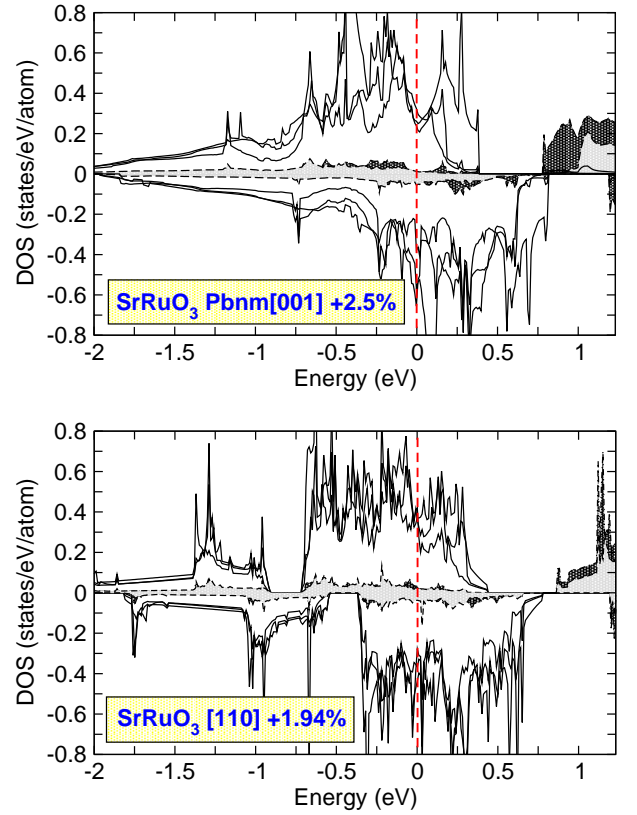


FIG. 12: Ru site projected partial DOS of SrRuO_3 in the vicinity of E_F . The electronic states with e_g symmetry are filled with gray color. Different orientations of the t_{2g} and e_g orbitals are plotted together without distinction in order to focus on the gaps which open when distortions are applied to the structure. (Top) DOS for the $e\text{-}Pbnm[001]$ structure of SrRuO_3 under tensile strain of 2.5%. The tensile strain reduces in-plane distortion of the oxygen octahedra, whereby the gap becomes smaller. (Bottom) DOS for the $e\text{-}Pbnm[110]$ structure. The strain is now also tensile, but 1.94%. There is another gap which opens about 0.8 eV (0.4 eV for spin-down) below the Fermi level. It happens because the $[110]$ orientation required additional distortion of the oxygen cages, forcing the t_{2g} electrons of Ru to split.

lous” orthorhombic shape of SrRuO_3 can be easily understood from simple geometrical considerations.

Two different orientations of the SrRuO_3 epitaxial films, $e\text{-}Pbnm[001]$ and $e\text{-}Pbnm[110]$, exhibit significant differences in their structural properties. The latter, unless there is no in-plane strain, has monoclinic symmetry, while the $[001]$ oriented film remains orthorhombic at any reasonable value of the strain.

SrRuO_3 exhibits significant magnetostructural coupling. Tensile strain reveals that in the non-magnetic state there is a distortion of Ru-Oz bonds which can be attributed to the change of Ru spin configuration, explaining the fact that this distortion does not appear in the magnetic state. The tilting and rotation help to preserve the shape of the octahedra when epitaxial strain is applied, whereby the magnetic orbital ordering is pre-

served. By suppressing the tilting under strain one could obtain a non-magnetic state of SrRuO₃.

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